COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

600352

APPLICATION FOR A STANDARD PATENT

I
We SHELL OIL COMPANY and MITSUI PETROCHEMICAL INDUSTRIES, LTD. of 900, Louisiana, Houston, Texas 77001, United States of America; of 2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo, Japan respectively.

hereby apply for the grant of a Standard Patent for an invention entitled:

"POLYMER BLEND FOR PACKAGING FILM, SHEET OR LAMINATE"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
054,569	UNITED STATES OF AMERICA	27th May 1987

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 30.5.90

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 14th day of April 19 88

To: THE COMMISSIONER OF PATENTS

H. W. Pimington
.....
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention

Insert title of invention.

entitled: "POLYMER BLEND FOR PACKAGING FILM, SHEET OR LAMINATE"

Insert full name(s) and address(es) of Declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I ~~We~~ Rand Shulman, Assistant General Counsel, of: SHELL OIL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America of: 900, Louisiana, Houston, Texas 77001, United States of America and

I, Kou Kunieda, Director of: MITSUI PETROCHEMICAL INDUSTRIES, LTD., a Japanese Body Corporate of:2-5, 3-chome, Kasumigaseki, Chiyoda-ku,Tokyo, Japan do solemnly and sincerely declare as follows :-

Cross out whichever of paragraphs 1(a) or 1(b) does not apply.

1(a) relates to application made by individual(s).

1(b) relates to application made by company; insert name of applicant company.

1(a) ~~I am / We are the applicant for the patent~~

or(b) I am authorized by SHELL OIL COMPANY

and I am authorised by MITSUI PETROCHEMICAL INDUSTRIES LTD.,

the applicant~~s~~ for the patent to make this declaration on ~~its~~ their behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply.

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2(a) ~~I am / We are the actual inventor~~

or(b) CHARLES C. HWO, a citizen of the United States of America of: 2710 Sugarwood Drive, Sugarland, Texas 77478, United States of America

~~is~~ the actual inventor of the invention and the facts upon which the applicant~~s~~ ~~is~~ are entitled to make the application are as follows :-

State manner in which applicant(s) derive title from inventor(s)

"The applicants would if a patent were granted upon an application made by the inventor , be entitled to have the patent assigned to it".

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~was~~ ~~were~~ made

in U.S.A. NO. 054,569 on the 27th May, 1987

by CHARLES C. HWO

in ..... on the .....

by .....

in ..... on the .....

by .....

4. The basic application..... referred to in paragraph 3 of this Declaration ~~was~~ ~~were~~ the first application..... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at Houston, Texas this 22nd day of April, 1988

Signature of Declarant(s) (no attestation required).

R.N. Shulman

Kou Kunieda

Note: Initial all alterations.

Declared at Tokyo, Japan
this 2nd May, 1988

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-14615/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 600352

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POLYMER BLEND FOR PACKAGING FILM, SHEET OR LAMINATE

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(56) Prior Art Documents
AU 588330 58952/86 C08L 23/20 B32B 27/06
AU 65769/86 C08L 23/16 23/08 23/10 B32B 27/32 C08J 5/18
AU 578364 57839/86 C08L 23/16, 23/20 B32B 27/32

(57) Claim

1. A blend suitable for use in packaging film or sheet and capable of providing a peelable seal, which blend comprises

(i) from 50 to 90 percent by weight of a copolymer of ethylene with an ethylenically unsaturated carboxylic acid;

(ii) from 5 to 25 percent by weight of a butene-1 homopolymer or copolymer of butene-1 with another olefin;and

(iii) from 5 to 45 percent by weight of a propylene homopolymer or copolymer of propylene with another olefin, the percentages being based on the combined weight of (i), (ii) and (iii).

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

CLASS INT. CLASS

APPLICATION NUMBER:
LODGED:

COMPLETE SPECIFICATION LODGED:
ACCEPTED:
PUBLISHED:

This document contains the amendments made under Section 49 and is correct for printing.

PRIORITY:

RELATED ART:

NAME OF APPLICANT: SHELL OIL COMPANY LTD. and MITSUI PETROCHEMICAL INDUSTRIES LTD.

ADDRESS OF APPLICANT: 900, Louisiana, Houston, Texas 77001, United States of America; and 2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo, Japan. respectively.

ACTUAL INVENTOR(S): CHARLES C. HWO

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1 Little Collins Stret
Melbourne 3000
Australia.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"POLYMER BLEND FOR PACKAGING FILM, SHEET OR LAMINATE"

The following statement is a full description of this invention, including the best method of performing it known to us:-

POLYMER BLEND FOR PACKAGING FILM, SHEET OR LAMINATE

The present invention relates to a polymer blend which can be used to provide a heat sealable wrapping or packaging film or sheet (for ease of reference mention will subsequently be made only to film) which is capable of forming a peelable seal. The seal is achievable either between two films of this kind, or between one film of this kind and a polypropylene packaging film without the need for an adhesive.

A peelable seal is defined to be the seal between two films produced by heat sealing or impulse sealing, the seal thus formed having the property of being able to open in the original plane of joining of the two films by the action of a pulling force, without wrenching off or tearing occurring in the material of the two films used to make up the seal. For the purposes of the present invention, the peelable seal must possess a mechanical resistance sufficient to maintain the integrity and the tight-seal properties of a packaging or wrapping round an article during storage and transport until such time as the packaging or wrapping is opened by the user of the article. The mechanical resistance of the peelable seal must be low enough to permit ready manual opening of the joint, i.e. without the use of any auxiliary instrument.

Many thermoplastic materials have been employed in the manufacture of films capable of forming peelable seals. For example, US-A-4,189,519 discloses a blend for producing a peelable heat seal comprising (1) 50 to 90 percent by weight of a copolymer of 80 to 96 percent by weight ethylene and 4 to 20 percent by weight of an ethylenically unsaturated ester, and (2) 10 to 50 percent by weight of a crystalline isotactic polybutylene. While capable of forming a peel seal, film of this blend will not bond to polypropylene without an adhesive although it will bond to high density polyethylene (HDPE) without the use of

adhesive.

US-A-3,900,534 discloses thermoplastic shrink films with good heat seal characteristics and good optical properties, but does not address the need for a peel seal film.

US-A-3,879,492 discloses blends of polybutylene + styrene-butadiene copolymer + low density polyethylene (LDPE) + HDPE + polyisobutylene.

US-A-4,539,263 discloses peel seals based on blends of comonomers and propylene/α-olefin copolymer, but does not provide disclosure directed to polybutylenes.

EP-A-213698 discloses blends of an ethylenic polymer, a butene-1 polymer and a propylene polymer, the amount of the butene-1 polymer being at least 50 percent by weight.

Various other references teach heat sealable films capable of forming peel seals, such as US-A-4,550,141, US-A-4,539,263 and US-A-4,414,053. However, none of these references discloses a blend, suitable for forming an intimate packaging film structure, as now disclosed herein.

There has been a long felt need for a wrapping or packing material having easy peelability at the seal and yet which will bond to a substrate without the aid of an adhesive.

According to the invention there is provided a polymer blend suitable for use in packaging film or sheet and capable of providing a peelable seal, which blend comprises

(i) from 50 to 90 percent by weight of a copolymer of ethylene with an ethylenically unsaturated carboxylic acid;

(ii) from 5 to 25 percent by weight of a butene-1 homopolymer or copolymer of butene-1 with another olefin; and

(iii) from 5 to 45 percent by weight of a propylene homopolymer or copolymer of propylene with another

olefin, the percentages being based on the combined weight of (i), (ii) and (iii).

(In this specification the term "polymer" is used to denote both homopolymers and copolymers).

In accordance with the invention it is not necessary to employ a separate tie layer adhesive and the equipment needed to dispose a tie layer adhesive on a substrate is no longer necessary. The invention recognises that conventional multilayer peelable seal films or sheets are comprised of substrates and peelable sealants which are generally not chemically compatible, whereas the present invention creates chemically compatible blends and peelable sealants. The invention avoids delamination layers when sealed layers are pulled apart. In some embodiments a tie adhesive can be utilized to bind incompatible substrates with sealants without the need for additional equipment to bind the adhesive between the sealant and the substrate. The invention reduces manufacturing costs for producing peelable seals.

The invention also provides a packaging film or sheet which is capable of forming a peel seal and which is of a blend of the invention. The invention further provides a laminar structure comprising a substrate to which is bonded, as by extrusion lamination, the packaging film or sheet of the invention. Using such films, sheets or laminates it is possible to form peel seals which have a nearly constant peel strength over an extended temperature range. Packages can be formed, as more consistent finished products, having seals of predictable and constant peel strength, despite inevitable variations in the heat seal temperatures used in forming the packages.

Thus, in accordance with the invention, it has been found that certain properties, including the peel seal characteristics of wrapping films or sheets, may be improved by fabricating films or sheets from blends containing 50 to 90 weight percent, preferably 55 to 70 weight percent of the

ethylene-carboxylic acid copolymer (i), 5 to 25 weight percent, preferably 10 to 20 weight percent of the butene-1 polymer (ii) and the propylene polymer (iii) in an amount of 5 to 45

weight percent (preferably 10 to 35 weight percent). Such films or sheets can be bonded to a substrate by coextrusion or extrusion lamination to form a laminate.

A particularly preferred blend of the invention is one which contains 65 percent by weight of the ethylene-carboxylic acid copolymer, about 15 percent by weight of the butene-1 polymer, and about 20 percent by weight of the propylene polymer.

The ethylene-carboxylic acid polymer is a copolymer of ethylene and an ethylenically unsaturated carboxylic acid, preferably an acid of the formula CHR=CRCOOH where each R, which may be the same or different, is hydrogen or alkyl, preferably C_1-C_4 alkyl. Suitable such acids include acrylic acid (AA), methyl acrylic acid (MAA), ethyl acrylic acid (EAA), butyl acrylic acid (BAA) and propyl acrylic acid (PAA).

The butene-1 polymer can be a butene-1 homopolymer and/or a copolymer of butene-1 with another olefin such as ethylene, propylene and alpha olefins having from 5 to 8 carbon atoms. The butene-1 polymer preferably is a homopolymer having a melt index of from 2 to 200. The butene-1 polymer can be stabilised with known stabilisers, such as "IRGANOX" (R.T.M.) 1010. Commercially available butene-1 polymers that can be used in accordance with the invention are PB 1560, PB 1520 and PB 0110 of Shell Chemical Company, Houston, Texas, USA.

The propylene polymer can similarly be a homopolymer or copolymer. Propylene copolymers will generally contain at least 25 weight percent of units derived from propylene.

The term "high density polyethylene" refers to a resin, such as DuPont Alathon® 7815 polyethylene, with a melt index of 0.25 to 6, and in particular about 0.45, and a density of from 0.944 g/cm^3 to 0.955 g/cm^3, and preferably 0.95 g/cm^3.

The term "tie layer adhesive" refers to an adhesive

which may be applied between a substrate, such as nylon or polycarbonate, and a layer of peelable sealant to bind the peelable sealant to the substrate.

The term "extrudate" refers to the substance which has been forced through the die of an extruder.

The term "peel sealability" refers to the sealed area of a film where the two parts are joined together. A film's peel sealability is measured by the degree of strength applied; such sealability can be measured by ASTM tensile strength testing method D-882.

The butene-1 polymer is preferably of a film-forming grade, and can, for example, be obtained commercially from the Shell Chemical Company or prepared as described in US-A-3,362,940. Desirably the polybutylene has a melt index of 0.1 to 500, preferably of 0.4 to 7, more preferably of 1 to 4 and most preferably of 2 $\pm$ 0.5.

The propylene polymer improves the processability of the blend.

The blend of the invention may be formed into an oriented, preferably biaxially oriented, or unoriented film or sheet by casting or film blowing. After fabrication the film or sheet can be heat sealed by sealing jaws at a preset temperature, pressure and dwell. The seal strength is tested by an Instron tensile tester at 25.4 cm/min (10"/min) crosshead speed. Maximum strength on a 2.54 cm (one inch) width strip was designated as peel seal strength.

These manufacturing techniques apply to film, but the blends can be used to form sheeting. Film refers to shaped plastics that are comparatively thin and have a maximum thickness of 0.025 mm (0.01 inch). Sheeting refers to shaped plastics having a thickness greater than 0.025 mm (0.010 inches).

The present invention also provides a laminar structure comprising a substrate to which is bonded a coating layer of the blend of the invention or a film or sheet of the blend. The peel seal coat, which consists of

the blend of the invention, can be coated or laminated onto the substrate. The substrate can be, for example, of nylon, high density polyethylene, aluminium foil, polycarbonate, polystyrene, polyurethane, polyvinyl chloride, polyester, polyacryonitrile or polypropylene. Except for high density polyethylene, nylon and the aluminium foil, the remaining substrates may require a tie layer adhesive to bond the blend layer to the substrate.

The laminated structure can be made by making two separate films that are then laminated. The individual films can be made by, for example, film blowing (melt extrusion with a circular die) or the casting method (a flat die-melt extrusion process). The films can be laminated by any suitable means, such as heat lamination. The laminated structure can also be made by coextrusion techniques, such as those described in US-A-2,480,998.

Melt extrusion with a flat die (casting) may be accomplished for thermoplastic polymers by using a flat die or slot die. The extrusion process starts with a polymer in a form that can be fed continuously into an extruder by means of a screw or pneumatic tube. Sometimes the polymers are combined with materials such as plasticizers, lubricants, stabilizers and colorants by means of, for example, Banbury mixers. The resulting mix is extruded through rod shaped dies and chipped into pellets. Pelletized polymer is fed into a screw conveyer into the end of a screw-type extruder and is heated and made into viscous fluid in a cylinder by means of a revolving, helical screw. The sheet emitting from the die is quenched on a temperature controlled chill roll. Finished films may be subject to a two-way stretching using continuous tenter-frame operations in biaxial orientation.

EXAMPLE 1

Polybutylene PB8340 ("DURAFLEX" obtainable from

Shell Chemical Company) having a melt index of about 4.0 dg/min (ASTM method D-1238 condition "E") and a density of 0.901 g/cm^3 was dry blended in a tumbler mixture with 75 w% of ethylene-acrylic acid copolymer (EAA) (Dow Primacor 1430) and 5 w% polypropylene (Shell PP5820) with a melt flow of 12. The resultant blend was coextruded with high density polyethylene (HDPE) (DuPont Alathon® 7815) at a die temperature of about 230°C into film of about 76 μm (3 mils) thick using a flat die (63 μm (2.5 mils) of HDPE and 13 μm (0.5 mils) of the remaining components). Peel sample strength was tested. The coextruded films were laminated together in face to face contact at 280 kPa (40 psi) pressure and a dwell time of about 0.5 seconds. After the film was cooled, strips having a unit width of 2.54 cm (1 inch) were cut from the film at locations across its width for testing of the seal strengths. Physical properties are given for the various strips at different temperatures in Table 1 below.

TABLE 1

Sealing Temperature °C (°F)	Peel Seal Strength kg/unit width (lb/inch)
127 (260)	0.36 (0.80)
138 (280)	0.82 (1.81)
149 (300)	1.11 (2.46)
160 (320)	1.69 (3.73)

As may be seen from Table 1, the film was tested for seal strength at different sealing temperatures. A satisfactory peel seal value is 0.45 kg/unit width (1.0 lb/in) or above. The results show, quite unexpectedly, that

the blend provides a mixture film which has good peel seal strength (a satisfactory peel seal value), good processability (does not adhere to the processing equipment), and will bond by coextrusion or extrusion lamination to a high density polyethylene substrate in a laminar structure without the need for an adhesive to achieve such bonding.

EXAMPLE 2

Polybutylene (PB 8340) as described in Example 1, was dry blended in a tumbler mixture with 80 weight percent (w%) of EAA (Dow PRIMACOR® 1430) and 5 w% polypropylene (PP 5820).

The resultant blend was coextruded with nylon 6 (Allied Chemical Company CAPRON® 8209F) at a die temperature of about 230°C into film about 89 μm (3.5 mil) thick (76 μm (3.0 mils) of nylon and 13 μm (0.5 mils) of the remaining components).

Peel sample strength was tested. The coextruded films were laminated together in face to face contact at 280 kPa (40 psi) pressure and a dwell time of about 0.5 seconds. After the film was cooled, strips having a unit width of 2.54 cm (one inch) were cut from the film at locations across its width for testing of seal strengths. Physical properties are given for the various strips at different temperatures in Table 2 below.

TABLE 2

Sealing Temperature ^{o}C (^{o}F)	Peel Seal Strength kg/unit width (lb/inch)
160 (320)	0.13 (0.29)
171 (340)	0.42 (0.92)
182 (360)	0.566 (1.25)
193 (380)	0.734 (1.62)

As may be seen from Table 2, the film was tested for seal strength at different sealing temperatures. From this example, it can be seen that the blend provides a film which has a satisfactory peel seal value and good processability and will bond by coextrusion to nylon in a laminar structure without the need for an adhesive tie layer to achieve such bonding.

The claims defining the invention are as follows:

1. A blend suitable for use in packaging film or sheet and capable of providing a peelable seal, which blend comprises

(i) from 50 to 90 percent by weight of a copolymer of ethylene with an ethylenically unsaturated carboxylic acid;

(ii) from 5 to 25 percent by weight of a butene-1 homopolymer or copolymer of butene-1 with another olefin;and

(iii) from 5 to 45 percent by weight of a propylene homopolymer or copolymer of propylene with another olefin, the percentages being based on the combined weight of (i), (ii) and (iii).

2. A blend according to claim 1, which comprises from 55 to 70 percent by weight of (i), from 10 to 20 percent by weight of (ii), and from 10 to 35 percent by weight of (iii).

3. A blend according to claim 1 or 2, which comprises about 65 percent by weight of (i), about 15 percent by weight of (ii) and about 20 percent by weight of (iii).

4. A blend according to claim 1, 2 or 3, wherein (i) is an ethylene/acrylic acid copolymer, ethylenemethyl acrylic acid copolymer, ethylene/ethyl acrylic acid copolymer, ethylene/butyl acrylic acid copolymer or ethylene/propyl acrylic acid copolymer.

5. A blend according to claim 1 substantially as described with reference to Example 1 or 2.

6. A packaging film or sheet which is capable of forming peel seals and is of a blend as claimed in any one of claims 1 to 5.

7. A packaging film or sheet according to claim 6 which is unoriented or which is biaxially oriented.

8. A laminar structure comprising a substrate to which is bonded a coating layer of a blend as claimed in any one of claims 1 to 5 or a packaging film or sheet as claimed in claim 6 or 7.

9. A laminar structure according to claim 8 wherein the substrate is of nylon, high density polyethylene or aluminium foil.

10. A laminar structure according to claim 8 substantially as herein described.

~~11. The hereinbefore described invention in all its new and useful aspects.~~

Dated this 14th day of April 1988

SHELL OIL COMPANY and MITSUI PETROCHEMICAL INDUSTRIES LTD.,
By their Patent Attorneys,
DAVIES & COLLISON.